5 Analysis of Variations in Ozone & Ozone Precursors

5.2 Ozone Precursor Trends in the SoCAB

Abstract

This chapter examines the long-term variations observed in concentrations of ozone, carbon monoxide, and the various forms of oxides of nitrogen (NO_X) in the South Coast Air Basin (SoCAB) by day of the week. For any hypothesis of a major factor contributing to the observed Weekend Effect to have validity, it must not only be consistent with the observed short-term (diurnal) variations but also the long-term variations in the parameters. Long-term variations (trends) are presented and examined for consistency with each hypothesis. These trending results are limited by the lack of good-quality continuous hydrocarbon data and the influence of year-to-year meteorological variations. These results indicate generally similar trends of carbon monoxide and oxides of nitrogen by day-of-week by monitoring site. However, the trends are not the same at all monitoring sites. Concentrations at some sites exhibit flat precursor trends (primarily in the eastern portion of the SoCAB); other sites exhibit slow to moderate downward trends. The trend of ozone concentrations was down at most sites but remained approximately flat at a few sites sites in the coastal area (e.g., Hawthorne, Long Beach). The ozone trend was flat at several other coastal sites until the 1990s when the trend became downward. An interesting feature of the ozone trends in the eastern SoCAB was that the weekday concentrations have decreased faster than the weekend concentrations (e.g., San Bernardino, Upland). These various trends are consistent with a faster rate of growth in the eastern basin than the western basin. This growth has diminished the rate of decline in emissions in the eastern basin. This trending analysis does not explicitly address the Carryover Hypothesis for the Weekend Effect. The results of the trending analysis do not support the Increased Weekend Emissions Hypothesis. The results are consistent with the VOC-Limited (NO_X-Disbenefit) and NO_X-Chemistry (NO_X-Timing) Hypotheses.

5.2.1 Introduction

A retrospective analysis of how ozone concentrations have changed over times with relatively different controls of ozone precursors provides an indication of how ozone concentrations will respond to future controls of ozone precursors. The South Coast Air Basin was chosen for this analysis because it experiences high ozone concentrations and has a large number of long-term monitoring sites in a variety of settings. By looking at trends by day-of-week, this analysis can isolate differences in emission patterns by day-of-week.

5.2.2 Methodology

Hourly ozone (O_3), carbon monoxide (CO), oxides of nitrogen (NO_X), nitric oxide (NO), and nitrogen dioxide (NO_2) concentration data were retrieved from ARB's air quality database for the summers (May – October) of 1980 through 1997. These data were averaged by pollutant, monitoring site, year, day-of-week, and hour. Ideally, each mean represents 26 data values. For trending, values based on less than 20 observations were removed from the analysis and the data were further averaged into six 4-hour periods of the day (PODs). For presentation purposes, the PODs for Tuesday, Wednesday, and Thursday were combined into a weekday mean; the Monday and Friday results were not plotted.

5.2.3 Results

The descriptions below are an attempt to characterize overall patterns common to multiple sites. A given site, in a given year, may lack some of the characteristics described.

5.2.3.1 Carbon Monoxide (CO)

CO concentrations are quite low during the summer and the POD results are plotted only for the mid-morning period (4 a.m. – 8 a.m. PST) for the core set of monitoring sites. The CO trends are incomplete at some monitoring sites because of site relocations or discontinued CO monitoring at sites with low concentrations in an attempt to cut costs. The mid-morning period is representative of the morning commute period and represents the initial conditions when photochemical reactions begin.

The CO trends are presented in Figures 5.2-1 through 5.2-X. Several features are apparent in many of the trend plots. First, the day-of-week relationships are very consistent with weekdays having the highest concentrations, Sundays having the lowest concentrations, and Saturdays having intermediate concentrations levels. The Saturday values appear to be closer to the Sunday values in central Los Angeles County and to be closer to the weekday values in the outlying areas.

Second, the year-to-year variations generally apply to all three days of the week and likely reflect local seasonal weather differences (e.g., higher frequency of fog or warm temperatures than normal). As one might expect based on the smaller sample size, the seasonal CO concentration values for Saturday and Sunday exhibit more variability than the weekday mean. Any consistent shift in the relationship between the days may reflect a change in day-of-week activity patterns.

Third, although further smoothing and testing are warranted for trending, we make the following observations with the knowledge that 1996 and 1997 were El Niño years with better dispersion of pollutants but also include an approximate 15 percent decrease in response to changes in gasoline composition. The overall pattern of CO concentrations appears to be flat since 1981 at Anaheim, Azusa, Los

Angeles, Lynwood, and Riverside; and down in the 1980s but flat in the 1990s at Burbank, Hawthorne, Long Beach, and possibly San Bernardino and Upland;

Lastly, about half of the monitoring sites had concentrations 2-3 times higher in 1980 than in subsequent years. This difference is much larger than the typical year-to-year variation and needs to be investigated further to determine the cause (e.g., calibration shift, meteorology, emission controls).

The CO trends do not specifically address the Weekend Effect Hypotheses. As a relatively long-lived, primary pollutant, the CO concentrations provide an indication of the overall seasonal influence of variable meteorological conditions. The trend plots do not provide supporting evidence for the Increased Weekend Emissions Hypothesis as weekend CO concentrations were lower throughout the day than weekday concentrations. The temporal resolution of the POD analysis may be too crude to address the Carryover Hypothesis. The CO trends do not shed additional light on the NO_X_Disbenefit and NO_X-Timing Hypotheses.

5.2.3.2 Oxides of Nitrogen (NO_X)

NO_X concentrations are quite low during the summer and the POD results are plotted only for the mid-morning period (4 a.m. – 8 a.m. PST) for the core set of monitoring sites. The NO_X trends are incomplete at some monitoring sites because of site relocations. The mid-morning period is representative of the morning commute period and represents the initial conditions when photochemical reactions begin.

The NO_X trends are presented in Figures 5.2-Y through 5.2-Z. Several features are apparent in many of the trend plots. First, the day-of-week relationships are very consistent with weekdays having the highest concentrations, Sundays having the lowest concentrations, and Saturdays having intermediate concentrations.

Second, unlike the CO values, the year-to-year variations do not generally apply to all three days of the week; apparently, the NO_X values do not solely reflect the changes in dispersion associated with local seasonal weather differences but also any variations in photochemistry paths and rates. Unlike the CO situation, the seasonal NO_X concentration values for the robust weekday mean exhibited almost as much variability as the Saturday mean and more variability than the Sunday mean.

Third, although further smoothing and testing are warranted for trending, we make the following observations with the knowledge that 1996 and 1997 were El Niño years with better dispersion of pollutants. The overall trend of NO_X concentrations on weekdays appears to be flat or slowly decreasing (however, Upland appears to have had a step increase in 1987). The overall trend of NO_X concentrations on weekends appears to be decreasing at a slightly faster rate than on weekdays.

NO_X concentrations for the late-morning POD are slightly lower and less variable than those for the mid-morning POD. Slight downward trends are generally evident

(Long Beach and Los Angeles trends are obvious) except in at sites in the eastern basin where the trends appear to be flat.

As a primary precursor of ozone, the NO_X trends can address the Weekend Effect Hypotheses. The trend plots do not provide supporting evidence for the Increased Weekend Emissions Hypothesis as weekend NO_X concentrations were lower throughout the day than weekday concentrations. The temporal resolution of the POD analysis may be too crude to address the Carryover Hypothesis; carryover of NO_X is not anticipated to be significant compared to carryover of ozone and volatile organic compounds (VOCs). The NO_X trends shed some light on the NO_X-Disbenefit and NO_X-Timing Hypotheses. Except for Long Beach, the mid-morning and late-morning period trends are very similar with the concentrations being lower in the late-morning than in the mid-morning POD. Thus, there is little evidence of a pattern towards increasing NO_X emissions in the late-morning or early-afternoon PODs for weekends or Sundays. Accordingly, this pattern does not provide evidence for the NO_X-limitation Hypothesis. Similarly, the mid-morning trends for weekdays and weekends do not appear to diverge over time. With the NO_X-Disbenefit Hypothesis, NO_X concentrations during the mid-morning POD should be decreasing faster on weekends than on weekdays. Accordingly, this pattern does not provide supporting evidence for the NO_X-Disbenefit Hypothesis.

5.2.3.3 Nitrogen Dioxide (NO_2)

NO_2 concentrations are lower during the summer than during the fall because the photolysis limits the accumulation of NO_2. POD results are plotted for the late-morning period (8 a.m. – noon PST) and the early-afternoon period (noon – 4 p.m. PST) for the core set of monitoring sites. The NO_2 trends are incomplete at some monitoring sites because of site relocations. The late-morning period is representative of the NO_2 build-up period and the “fuel” available for ozone generation. The early-afternoon period represents the conditions when ozone production is greatest.

The NO_2 trends are presented in Figures 5.2-Z through 5.2-ZZ. Several features are apparent in many of the trend plots. First, the day-of-week relationships are very consistent with weekdays having the highest concentrations, Sundays having the lowest concentrations, and Saturdays having intermediate concentrations.

Second, the year-to-year variations are generally smaller than observed for the NO_X values, as might be expected. The seasonal NO_2 concentration values for the robust weekday mean exhibited almost as much variability as the Saturday mean and more variability than the Sunday mean.

Third, although further smoothing and testing are warranted for trending, we make the following observations with the knowledge that 1996 and 1997 were El Niño years with better dispersion of pollutants. The overall trends of NO_2 concentrations are downward at most sites in the western and central SoCAB and flat in the eastern portion of the basin. The decline is fastest at the Long Beach site. At a few sites (e.g., Azusa) the weekday and Saturday trends appear flat in the 1990s.

NO_2 concentrations for the early-afternoon POD, although slightly lower than concentrations for the late-morning POD, exhibit a similar pattern with varying degrees of downward trends in the western SoCAB and somewhat flat trends in the eastern basin.

As the source of oxygen atoms for ozone formation, the NO_2 trends can address the Weekend Effect Hypotheses. The trend plots do not provide supporting evidence for the Increased Weekend Emissions Hypothesis as weekend NO_2 concentrations were lower throughout the day than weekday concentrations. The temporal resolution of the POD analysis may be too crude to address the Carryover Hypothesis; carryover of NO_2 is not anticipated to be significant compared to carryover of ozone and volatile organic compounds (VOCs). Although year-to-year variability is still significant for NO_2, the trends appear similar by day-of-week and period-of-day. Thus, the NO_2 trends do not shed additional light on the NO_X-Disbenefit and NO_X-Timing Hypotheses.

5.2.3.4 Ozone (O_3)

O_3 concentrations are plotted for the late-morning period (8 a.m. – noon PST) and the early-afternoon period (noon – 4 p.m. PST) for the core set of monitoring sites. The late-morning period is representative of the O_3 build-up period and the early-afternoon period represents the conditions when O_3 concentrations peak.

The O_3 trends are presented in Figures 5.2-AA through 5.2-AB. Several features are apparent in many of the trend plots. First, the day-of-week relationships are reversed from those of CO and NO_X; weekdays consistently have the lowest concentrations, Sundays have the highest concentrations, and Saturdays have intermediate concentrations. The differences between the days of the week become smaller from the late-morning period to the early-afternoon period.

Second, the year-to-year variations in O_3 concentrations are generally smaller for the robust weekday mean than the Saturday and Sunday means.

Third, although further smoothing and testing are warranted for trending, we make the following observations with the knowledge that 1996 and 1997 were El Niño years with better dispersion of pollutants. The overall late-morning trend of O_3 concentrations is downward at most sites; Hawthorne, Long Beach, and Lake Gregory are the exceptions with flat O_3 trends.

The average O_3 concentrations for the early-afternoon POD, are a few parts per hundred million higher than the concentrations for the late-morning POD. One difference between the late-morning and the early-afternoon PODs however is that sites in the eastern portion of the basin tend to have the highest ozone concentrations on Saturday in the early-afternoon but Sunday tended to have the highest concentrations in the late-morning POD. Thus, to some extent it appears that the O3 concentrations at some sites continue to increase more from late morning into early afternoon on Saturdays than on Sundays in the eastern portion of the basin. It also appears that weekday concentrations have declined faster than weekend (especially Sunday) concentrations in the eastern portion of the air basin where the peak concentrations tend to occur. The relative difference between days of the week is smallest (weekday concentrations are often higher than the Sunday concentrations) at Lake Gregory, one of the high ozone sites in the basin. The downward trend in concentrations on Sundays, and to some extent on Saturdays, is less than on weekdays.

Except for Lake Gregory, early-morning O_3 concentrations are low (presumably due to scavenging by NO and deposition), the concentrations are very similar by day-of-week, and the trends are flat. Mid-morning O_3 concentrations on the other hand begin to separate by day-of-week. At many locations, the separation appears due to greater NO titration on weekdays than on Saturdays than on Sundays as concentrations decrease from early-morning to mid-morning. At other locations where NO emissions are not large, the mid-morning O_3 concentrations on Sunday have already begun increasing. This early increase in ozone concentrations on Sundays is consistent with the diurnal profiles in the previous chapter and indicates that ozone formation is exceeding scavenging by NO. This pattern is consistent with the NO_X-disbenefit hypothesis.

5.2.4 Conclusions

Although simple and qualitative, this initial characterization of ozone and ozone precursor trends by period of the day yielded fairly consistent results despite the year-to-year “noise” caused by meteorological variations.

The trends by day-of-week and period-of-day do not support the Increased Emissions Hypothesis. Although there is some evidence of boundary-layer carryover of NO_X on Saturday mornings in the early years, the day-of-week differences became small in the 1990s. The trend analyses are too crude to assess the presence and significance of carryover aloft. The mid-morning trend analyses also provide supporting evidence for the NO_X-disbenefit Hypothesis. The late-morning and early-afternoon trend analyses did not provide supporting evidence for the NO_X-timing Hypothesis.

5.2.5 Recommendations

The analysis identified some large, stepwise changes which warrant further investigation and illustrate the importance of have a good quality assurance program and high precision instruments as ambient concentrations approach detection limits. Our recommendations are as follows:

1) Perform a thorough review of the data for outliers and calibration changes before averaging the various data.

2) Use techniques to smooth or to minimize some of the year-to-year variations in meteorology and its influence on ambient concentrations.

3) Although the continuous hydrocarbon monitors in the SoCAB were removed from service at the end of 1995 and the methane and non-methane hydrocarbon data from them were not reliable, trends similar to those above should be generated for total hydrocarbon (THC) concentrations and THC/NO_X ratios. Hydrocarbons are important precursors to ozone and a good understanding of their diurnal and long-term variations could yield valuable insights into the Weekend Effect for ozone.

5.3 References